Communication

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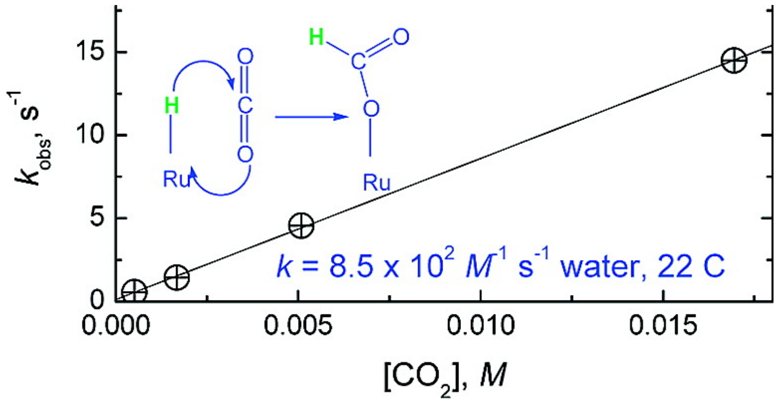
J. Am. Chem. Soc., **2007**, 129 (33), 10108-10109• DOI: 10.1021/ja074158w • Publication Date (Web): 28 July 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Rapid Transfer of Hydride Ion from a Ruthenium Complex to C_1 Species in Water

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Water is recognized as a desirable solvent for catalysis[1,2] and as a promising raw material for solar generation of fuels;[3] however, relatively few kinetics and mechanism studies of C_1 reduction reactions[4] in aqueous media have been reported. The observation of Konno et al.[5] that high solvent acceptor number[6] (AN) enhances the rate of hydride transfer from Ru(terpy)(bpy)H^+ (RuH^+, terpy = 2,2′,6′,2″-terpyridine; bpy = 2,2′-bipyridine, Chart 1) to carbon dioxide in organic solvents has led us to characterize this reaction in water. We find that solvent water (AN = 55) accelerates the CO_2 reaction rate by more than 4 orders of magnitude compared to acetonitrile (AN = 18.9) and that water also promotes the related reductions of C_1 species carbon monoxide and formaldehyde by RuH^+.

The lowest energy electronic absorption of RuH^+, a Ru(II)-to-terpy charge transfer at 500 nm in water, shifts to shorter wavelength upon hydride transfer to C_1. The kinetics of the hydride-transfer reactions were followed by UV−vis spectroscopy, with both CO_2 and CH_2O requiring stopped-flow methods. All exhibited second-order rate laws, $-d[RuH^+]/dt = k_A[RuH^+][A]$ M s^{-1} where A is the hydride acceptor, CO_2 (see Figure 1), CO, or CH_2O.[7]

Product solutions were characterized by electrospray ionization mass spectrometry (ESI-MS), and assignments were confirmed by comparison with authentic samples prepared by other methods.[7] With CO_2 reactant, product $m/z = 536$ is assigned to ^{102}Ru(terpy)(bpy)[OCH(O)]$^+$. For CO, the $m/z = 351.6$ peak is assigned as ^{102}Ru(terpy)(bpy)(OCH_2(OH))[PF_6](H_3O)$^{2+}$ ($z = 2$, $m = 703$). With formaldehyde as reactant, $m/z = 522$ is ^{102}Ru(terpy)(bpy)(OCH_3)$^+$. Scheme 1 summarizes the reaction sequence.

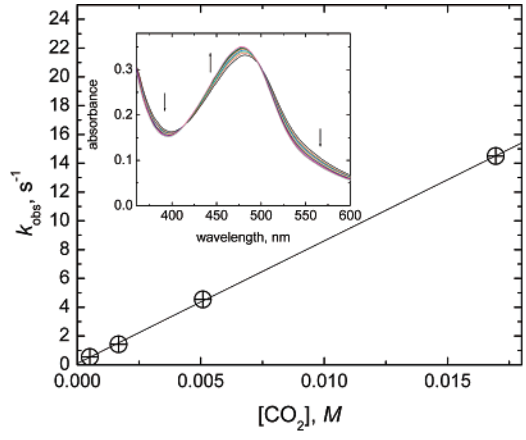


Figure 1. The pseudo-first-order rate constant for reaction of Ru(terpy)(bpy)H^+ with CO_2 at pH 5.8 as a function of CO_2 concentration. Inset: Scans taken every 500 ms with 1.5% saturated CO_2 (0.45 mM, first point).

Chart 1

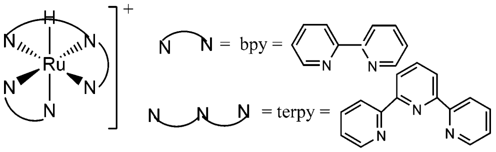
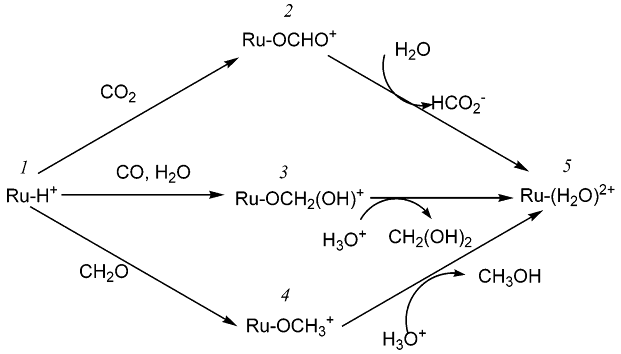


Table 1. Rate Constants and Products for the Hydride Transfer to Acceptor A

parameter	A: CO_2	A: CO	A: CH_2O
k_A, M^{-1} s^{-1} [a]	8.5×10^2	0.7	$\sim 1 \times 10^6$
λ_{max}, nm[b]	490	487	486
m/z product[c]	536 (100%)	351.6 (85%)	522 (30%)[d]
k_{aq}, s^{-1}	0.4×10^{-3} [e]	1.4×10^{-4} [e]	8.8×10^{-4} [f]

[a] Rate constant for hydride transfer to A (Scheme 1). [b] Position of lowest energy MLCT band of hydride adduct of A. [c] Value in parenthesis is relative intensity at its maximum (usually first trace). [d] The product methanol complex manifested as an intense peak at $m/z = 523$ only when the collision energy was reduced to 25%. [e] Rate of aquation at pH 5.3. [f] Rate of aquation in water, no buffer added.

Scheme 1



In contrast to previous studies of hydride transfer to free[2] or metal-bound C_1 species such as $Ru^{II}(bpy)_2(CO)(C_1)$,[8−11] for each hydride-transfer reaction studied here the initial product implicated is the O-bonded hydride adduct: formate ion RuOCHO$^+$ (2), formaldehyde hydrate RuOCH_2(OH)$^+$ (3), or methanol RuOCH_3^+ (4). This assignment is consistent with the ESI MS, UV−vis spectrum, comparison with known samples, and the relatively rapid transformation to Ru−OH_2^{2+} (λ_{max} 477, pK_a 10).[12] Results are summarized in Table 1. The importance of the Lewis acidity of the anhydride or keto form of the C_1 acceptor to its ability to accept hydride ion is striking. For CO_2, a pH-jump experiment[13,14] established that reaction of RuH^+ with CO_2 is >50 times greater than with HCO_3^-. For CO, reaction with its hydrate, formate ion, is $<10^{-5}$ M^{-1} s^{-1}, at least one-million times slower than the reaction with CO. Similarly for formaldehyde, the minor species H_2CO[15,16] was at least 10^5 times more reactive than its dominant hydrate form.

We bracket the hydricity[17] of this Ru(II) hydride using our kinetic data. The intercept of the plot of k_{obs} versus [CO_2] is 0.1 s^{-1}, and the slope is 8.5×10^2 M^{-1} s^{-1}. Then the rate constant for the reverse

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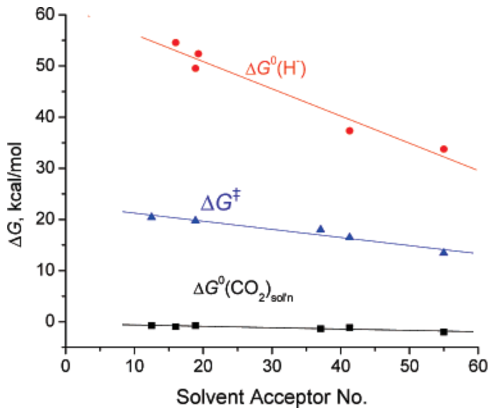
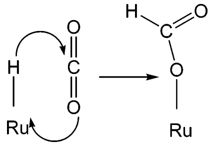


Figure 2. Free energies of hydride-ion formation ($\Delta G^0(H^-)$) (circles),[19] free energy of activation $\Delta G^‡$ for hydride transfer from RuH^+ to CO_2 (triangles),[5] and ($\Delta G^0(CO_2)_{soln}$), the free-energy of solution[5] of CO_2 (squares), as a function of solvent acceptor number.[6]

reaction is $\leq 0.1\ s^{-1}$, and $K_{A,12}$ for the hydride transfer (from the ratio of forward and reverse constants) is $\geq 10^4\ M^{-1}$ and $\Delta G^0 \leq -5$ kcal/mol. Since the hydricity of formate in water is 23 kcal/mol[18] (based on $pK_a(H_2) = 22$[19] rather than the commonly used, earlier value 31), the hydricity of Ru(terpy)(bpy)H^+ in water is ≤ 18 kcal/mol.

As discussed previously[5,20] for reaction of CO_2 with RuH^+ and Re(bpy)$(CO)_3$H, these reactions involve hydride transfer via transition states (Scheme 2) for CO_2.

Scheme 2



The reactions cannot involve Ru binding of O, followed by transfer of H^-, since substitution reactions at the Ru(II) center are many orders of magnitude too slow[21] (for binding of acetonitrile, $k = 0.3 \times 10^{-4}\ M^{-1}\ s^{-1}$)[18] to account for the observed rates.

On the basis of the work presented, it is evident that water is an excellent solvent for the hydride transfer to the free C_1 acceptors. It is of great interest to understand the basis of this reactivity enhancement, which is much greater than expected from dielectric continuum considerations.[5,20] We compare the effect of solvent acceptor number on thermodynamic and kinetic parameters in Figure 2.

Acceptor number reflects the electrophilic properties of the solvent; with increasing AN, the negative charge on the hydride ligand is increasingly stabilized. The trend observed here for $\Delta G^0(H^-)$ has also been found for chloride ion.[6] The plot in Figure 2 strongly suggests that the thermodynamics of formation of the hydride ion is responsible for the exceptional solvent sensitivity of the hydride-transfer rate to solvent acceptor number and encourages us to explore the scope of this reactivity enhancement in future experiments with other metal-hydride donors and both metal-bound and free hydride acceptors.

Acknowledgment. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10884 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank M. Bullock, D. DuBois, E. Fujita, and J. Muckerman for extended discussions that led to this work, S. Lymar and N. Sutin for helpful comments on its interpretation, and N. Shaikh, K.-W. Huang, and D. Polyansky for help with the experiments.

Supporting Information Available: Experimental details, kinetics and products for reaction with CO_2, CO, and CH_2O, the hydricity of formate ion. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The hydride complex [**1**][PF_6] was prepared as described[5]: ^1H NMR (DMSO-d_6 $\delta = -14.7$; IR (KBr pellet) ν_H 1827 cm^{-1}, ν_D 1292 cm^{-1}; UV−vis 500 nm ($8.5 \times 10^3\ M^{-1}\ cm^{-1}$); ESI MS in acetonitrile *m/z* 492.2 [Ru(terpy)(bpy)H^+ ^{102}Ru, relative intensity 100% in *m/z* range 200−1000]. The hydride complex undergoes very rapid exchange with the deuterons of D_2O, CD_3OD, and C_2D_5OD, probably via a dihydrogen complex, and reacts with acid ($k < 10^3\ M^{-1}\ s^{-1}$) to yield dihydrogen (yield $\geq$ 60%); the kinetics and mechanism of these reactions are currently under study. Manipulations were carried out under dim light. As noted by Konno et al.,[5] the hydride complex is not oxygen sensitive, but must be rigorously protected from the carbon dioxide in air. Thus reagents were prepared under argon with freshly drawn mill-Q water and transferred with use of syringe techniques. Kinetics runs were carried out with 0.03−0.1 mM RuH^+ and the C_1 species usually in at least 10-fold excess at 22 °C. Experiments with CO used 100% and 50% CO/50% Ar-saturated solutions in water (0.94 and 0.47 mM, respectively). Commercial CO_2/Ar mixtures were used to vary the [CO_2], and the reactions were monitored by diode array on an Applied Photophysics stopped-flow spectrometer. Mass spectra were simulated using Isotope Distribution Calculator (http://www2.sisweb.com/mstools/isotope.htm) and monitored on a Thermo Finnigan LCQ MS. Samples for comparison with the products of the C_1 reactions were synthesized as follows: CO_2 was reacted with RuH^+ in methanol to give the O-bonded formate complex as established by X-ray crystal structure by Konno et al.[5] The formaldehyde adduct was prepared through reaction of Ru(terpy)(bpy)$(H_2O)^{2+}$ with formaldehyde at pH 9 (borate buffer); this reaction is relatively rapid, evidently involving Ru−OH attack on CH_2O (substitution on carbon, not ruthenium). The methanol complex was prepared by dissolving Ru(terpy)(bpy)$(H_2O)[PF_6]_2$ in methanol for an hour, followed by evaporation to dryness. The digitized absorbance−time data from kinetics runs were least-squares-fit to an exponential function using Origin.
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JA074158W